I. RESTRICTED ROTATION IN ARYL OLEFINS
II. STRUCTURE OF LEUCENOL

BY

ARTHUR WILLIAM ANDERSON

B.S., Northwestern University, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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I. RESTRICTED ROTATION IN ARYL OLEFINS

INTRODUCTION

The first true aryl olefin to be resolved involved a synthesis that Mills [1] could not extend to the preparation of closely related compounds. Adams and Miller [2] synthesized a resolvable aryl olefin by an entirely different method. It was a purpose of this investigation to prepare by the same synthesis and attempt to resolve some analogs and derivatives of this latter compound. Other methods of synthesis, which would be necessary in the preparation of other related aryl olefins, were to be investigated so that a study of the effect of different groups around the point of restricted rotation could be made.

DISCUSSION OF EXPERIMENTAL

Derivatives of β-Chloroacrylic Acid.—Restricted rotation was demonstrated in β-chloro-β-(2,4,6-triethyl-3-bromophenyl)-α-methylacrylic acid, β-chloro-β-(2,4,6-triethyl-3-bromophenyl)-N-acrylyl glycine, β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methyl-N-acrylyl glycine and β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-N-acrylyl glycine by resolving them into their optically active isomers.

The enantiomorphs of the last compound mentioned were the only ones able to be racemized by boiling in *n*-butanol. The half-life of the active forms was found to be one hundred thirty-three minutes, whereas the half-life of the compound identical, except for the absence of the glycine group, was found to be two hundred minutes. It is believed that the explanation of this lies in the fact that the presence of a large group like glycine might distort the valence angles so that there would actually be less hindrance than without it.

β-(1-Naphthyl)-acrylic Acids.—The two geometric isomers of β-(8-bromo-2,7-dimethoxynaphthyl)-α-methylacrylic acid were synthesized.[3,4] Attempts to resolve the more-soluble form with brucine and quinine and the less-soluble form with quinine resulted in salts which had constant rotations. The acids obtained by decomposition of these salts were inactive. Since Stuart models show that these compounds are resolvable, this indicates the unreliability of these models in predicting restricted rotation.

Mesitylacetic Acids.[4]—In this series propio- and isobutyromesitylene were converted to 3-(α-chloropropenyl)- and 3-(α-chloro-

isobutenyl)-2,4,6-trimethylphenylacetic acids, respectively. The ketone in each case was first converted to the unsaturated chloro derivative, which was then chloromethylated in the mesitylene nucleus. This chlorine was replaced with a nitrile group and in turn was converted to the amide and finally the acid.

II. STRUCTURE OF LEUCENOL

INTRODUCTION

In 1937, Mascré [5] isolated a crystalline solid from the seed of *Leucaena glauca Benth.* His elementary analysis showed that the compound had an empirical formula $C_4H_5O_2N$. His examination of the compound indicated the presence of a carboxyl, a phenolic hydroxyl, and an amino group.

DISCUSSION OF EXPERIMENTAL

A new method of extraction, superior to the one used by Mascré, has been developed. The remainder of his work was checked and confirmed. Attempts to acetylate the compound were unsuccessful. By determination of amino nitrogen the formula was shown to be at least twice the empirical formula found by Mascré.

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[5] Mascré, Compt. rend., 204, 890 (1937).

VITA

The writer was born in Chicago, Illinois, on April 14, 1916. He attended the public schools of that city and was graduated from Nicholas Senn High School in 1934. In 1937 he obtained the degree of Bachelor of Science from Northwestern University. He entered the graduate school of the University of Illinois in the same year. During the years 1937-1940 he was a teaching assistant in chemistry there. He held the Eastman Kodak Fellowship during the year 1940-1941.

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